

08/414,415  
APS (USPAT)  
11-5-96

L1 121 S 526/147/CCLST  
L2 12 S L1 AND METHYL ACRYLATE  
L3 0 S L2 AND "CU(I)BR"  
L4 0 S L2 AND "CU(I) "  
L5 1 S L2 AND BIPYRIDINE  
L6 1 S L1 AND BIPYRIDINE  
L7 72 S DIBROMOXYLENE  
L8 0 S L2 AND L7  
L9 0 S L1 AND L7  
L10 0 S L5 AND L7  
L11 0 S L6 AND L7

=> d 15

1. 4,716,205, Dec. 29, 1987, Nickel-catalyzed polymerization of ethylene; Ulrich Klabunde, 526/115, 117, 118, 119, 121, 124.1, 124.2, 126, 127, 128, 135, 141, 142, 144, \*\*147\*\*, 149, 154, 155, 160, 161, 171, 352 [IMAGE AVAILABLE]

08/414,415  
STN/CAS (CA)  
11-6-96

=> s atom transfer radical polymerization

207788 ATOM  
416982 TRANSFER  
152211 RADICAL  
163919 POLYMERIZATION

L1 12 ATOM TRANSFER RADICAL POLYMERIZATION  
(ATOM(W) TRANSFER(W) RADICAL(W) POLYMERIZATION)

=> s group transfer radical polymerization

741444 GROUP  
416982 TRANSFER  
152211 RADICAL  
163919 POLYMERIZATION

L2 0 GROUP TRANSFER RADICAL POLYMERIZATION  
(GROUP(W) TRANSFER(W) RADICAL(W) POLYMERIZATION)

=> s l1 and methyl acrylate

414756 METHYL  
95290 ACRYLATE  
8628 METHYL ACRYLATE  
(METHYL(W) ACRYLATE)

L3 4 L1 AND METHYL ACRYLATE

=> s l3 and "Cu(I)"

432409 "CU"  
2559473 "I"  
6463 "CU(I)"  
("CU"(W) "I")

L4 1 L3 AND "CU(I)"

=> d l4 bib abs

L4 ANSWER 1 OF 1 CA COPYRIGHT 1996 ACS

AN 123:257535 CA

TI Controlled/"Living" Radical Polymerization. Halogen Atom  
Transfer Radical Polymerization Promoted  
by a Cu(I)/Cu(II) Redox Process

AU Wang, Jin-Shan; Matyjaszewski, Krzysztof

CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA,  
15213, USA

SO Macromolecules (1995), 28(23), 7901-10  
CODEN: MAMOBX; ISSN: 0024-9297

DT Journal

LA English

OS CJACS

AB An extension of atom transfer radical addn., ATRA, to atom transfer radical polymn., ATRP, provided a new and efficient way to conduct controlled/. By using a simple alkyl halide, R-X (X = Cl and Br), as an initiator and a transition metal species complexed by suitable ligand(s), Mtn/Lx, e.g., CuX/2,2'-bipyridine, as a catalyst, ATRP of vinyl monomers such as styrenes and (meth)acrylates proceeded in a living fashion, yielding polymers with d.p. predetd. by .DELTA.[M]/[I]0 up to Mn .apprxeq. 105 and low polydispersities, 1.1 < Mw/Mn < 1.5. The participation of free radical intermediates was supported by anal. of the end groups and the stereochem. of the polymn. The general principle and the mechanism of ATRP are elucidated. Various factors affecting the ATRP process are discussed.

=> d his

(FILE 'HOME' ENTERED AT 09:24:49 ON 06 NOV 96)  
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L1 12 S ATOM TRANSFER RADICAL POLYMERIZATION  
L2 0 S GROUP TRANSFER RADICAL POLYMERIZATION  
L3 4 S L1 AND METHYL ACRYLATE  
L4 1 S L3 AND "CU(I)"

=> d l3 bib abs 1-4

L3 ANSWER 1 OF 4 CA COPYRIGHT 1996 ACS  
AN 125:248559 CA  
TI Kinetic studies of atom transfer radical  
polymerization of methyl acrylate  
AU Paik, Hyun-jong; Matyjaszewski, Krzysztof  
CS Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA,  
15213, USA  
SO Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1996), 37(2),  
274-275  
CODEN: ACPPAY; ISSN: 0032-3934  
DT Journal  
LA English  
AB Kinetic studies of the polymn. of Me acrylate with a homogeneous and  
heterogeneous catalytic system are described and related to the  
evolution of mol. wts. and polydispersities with conversion.

L3 ANSWER 2 OF 4 CA COPYRIGHT 1996 ACS  
AN 123:257535 CA

TI Controlled/"Living" Radical Polymerization. Halogen Atom  
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 AU Wang, Jin-Shan; Matyjaszewski, Krzysztof  
 CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA,  
 15213, USA  
 SO Macromolecules (1995), 28(23), 7901-10  
 CODEN: MAMOBX; ISSN: 0024-9297  
 DT Journal  
 LA English  
 OS CJACS  
 AB An extension of atom transfer radical addn., ATRA, to atom transfer  
 radical polymn., ATRP, provided a new and efficient way to conduct  
 controlled/. By using a simple alkyl halide, R-X (X = Cl and Br),  
 as an initiator and a transition metal species complexed by suitable  
 ligand(s), M<sub>tn</sub>/L<sub>x</sub>, e.g., CuX/2,2'-bipyridine, as a catalyst, ATRP of  
 vinyl monomers such as styrenes and (meth)acrylates proceeded in a  
 living fashion, yielding polymers with d.p. predetd. by  
 .DELTA.[M]/[I]<sub>0</sub> up to Mn .apprxeq. 10<sup>5</sup> and low polydispersities, 1.1  
 < Mw/Mn < 1.5. The participation of free radical intermediates was  
 supported by anal. of the end groups and the stereochem. of the  
 polymn. The general principle and the mechanism of ATRP are  
 elucidated. Various factors affecting the ATRP process are  
 discussed.

L3 ANSWER 3 OF 4 CA COPYRIGHT 1996 ACS  
 AN 123:229035 CA  
 TI "Living"/Controlled Radical Polymerization. Transition-Metal-  
 Catalyzed Atom Transfer Radical  
 Polymerization in the Presence of a Conventional Radical  
 Initiator  
 AU Wang, Jin-Shan; Matyjaszewski, Krzysztof  
 CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA,  
 15213, USA  
 SO Macromolecules (1995), 28(22), 7572-3  
 CODEN: MAMOBX; ISSN: 0024-9297  
 DT Journal  
 LA English  
 OS CJACS  
 AB A novel type of atom transfer radical polymn., ATRP, initiated with  
 AIBN/cuIICl<sub>2</sub>/bpy affords the bulk polymn. of styrene at 130.degree.  
 in a "living"/controlled manner, similar to the one with R-X/CuI/bpy  
 reported earlier. Moreover, a "living"/controlled ATRP of Me  
 acrylate at 130.degree. was accomplished, when a catalytic amt. of  
 AIBN (1% molar equiv.) was combined with 2-chloropropionitrile

(initiator) in the presence of bpy/CuIICl<sub>2</sub>.

L3 ANSWER 4 OF 4 CA COPYRIGHT 1996 ACS  
AN 122:315212 CA  
TI Controlled/"living" radical polymerization. atom  
transfer radical polymerization in the  
presence of transition-metal complexes  
AU Wang, Jin-Shan; Matyjaszewski, Krzysztof  
CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA,  
15213, USA  
SO J. Am. Chem. Soc. (1995), 117(20), 5614-15  
CODEN: JACSAT; ISSN: 0002-7863  
DT Journal  
LA English  
OS CJACS-IMAGE; CJACS  
AB Atom transfer radical polymn. of styrene and Me acrylate is  
investigated using 1-phenylethyl chloride as a chlorine atom  
transfer precursor (initiator) and CuCl/2,2'-bipyridine complex as a  
chlorine atom transfer promoter (catalyst). The "living" radical  
polymn. of styrene alone generates polymers with predetd. mol. wt.  
up to Mn .apprxeq. 105 and with narrow mol. wt. distribution. Block  
copolymers of styrene and Me acrylate are also synthesized using the  
same technique.

=> d 11 bib abs 1-12

L1 ANSWER 1 OF 12 CA COPYRIGHT 1996 ACS  
AN 125:248559 CA  
TI Kinetic studies of atom transfer radical  
polymerization of methyl acrylate  
AU Paik, Hyun-jong; Matyjaszewski, Krzysztof  
CS Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA,  
15213, USA  
SO Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1996), 37(2),  
274-275  
CODEN: ACPPAY; ISSN: 0032-3934  
DT Journal  
LA English  
AB Kinetic studies of the polymn. of Me acrylate with a homogeneous and  
heterogeneous catalytic system are described and related to the  
evolution of mol. wts. and polydispersities with conversion.

L1 ANSWER 2 OF 12 CA COPYRIGHT 1996 ACS  
AN 125:222588 CA  
TI Branched and hyperbranched macromolecules by atom

transfer radical polymerization

AU Gaynor, Scott G.; Edelman, Shane Z.; Kulfan, Anthony; Matyjaszewski, Krzysztof  
CS Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213, USA  
SO Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1996), 37(2), 413-414  
CODEN: ACPPAY; ISSN: 0032-3934  
DT Journal  
LA English  
AB Homopolymn. of p-chlorostyrene (I) in the presence of CuCl and 2,2'-bipyridyl gave hyperbranched polystyrene, which could copolymd. with Bu acrylate to grow linear chains off the hyperbranched macromol. The prepn. of branched polymers was demonstrated by copolymn. of I with styrene and with Me methacrylate.

L1 ANSWER 3 OF 12 CA COPYRIGHT 1996 ACS

AN 125:222540 CA

TI Kinetic investigation of the atom transfer  
radical polymerization of styrene in homogeneous  
systems

AU Xia, Jianhui; Matyjaszewski, Krzysztof  
CS Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213, USA  
SO Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1996), 37(2), 513-514  
CODEN: ACPPAY; ISSN: 0032-3934  
DT Journal  
LA English  
AB The kinetics of atom transfer radical polymn. of styrene under homogeneous conditions was investigated.

L1 ANSWER 4 OF 12 CA COPYRIGHT 1996 ACS

AN 125:222482 CA

TI Principle and feature of atom transfer  
radical polymerization

AU Luo, Ning; Ying, Shengkang  
CS Inst. of Material Sci. and Eng., East China Univ. of Sci. and Technol., Shanghai, 200237, Peop. Rep. China  
SO Hecheng Xiangjiao Gongye (1996), 19(5), 299-302  
CODEN: HXGOEA; ISSN: 1000-1255  
DT Journal; General Review  
LA Chinese  
AB A review with 12 refs. on principle, classification, feature, and application of atom transfer radical polymn.

L1 ANSWER 5 OF 12 CA COPYRIGHT 1996 ACS

AN 124:344280 CA

TI Polymers with very low polydispersities from atom transfer radical polymerization

AU Patten, Timothy E.; Xia, Jianhui; Abernathy, Teresa; Matyjaszewski, Krzysztof

CS Dep. Chem., Carnegie Mellon Univ., Pittsburgh, PA, 15213, USA

SO Science (Washington, D. C.) (1996), 272(5263), 866-868

CODEN: SCIEAS; ISSN: 0036-8075

DT Journal

LA English

AB A radical polymn. process that yields well-defined polymers normally obtained only through anionic polymn. is reported. Atom transfer radical polymn. of styrene was conducted with several solubilizing ligands for the copper(I) halides: 4,4'-di-tert-Bu-, 4,4'-di-n-heptyl-, and 4,4'-di-(5-nonyl)-2,2'-dipyridyl. The resulting polymns. have all of the characteristics of a living polymn. and displayed linear semilogarithmic kinetic plots, a linear correlation between the no.-av. mol. wt. and the monomer conversion, and low polydispersity (ratio of the wt.-av. to no.-av. mol. wts. of 1.04 to 1.05). Similar results were obtained for the polymn. of acrylates.

L1 ANSWER 6 OF 12 CA COPYRIGHT 1996 ACS

AN 124:318011 CA

TI Radical polymerization yielding polymers with Mw/Mn .apprx.1.05 by homogeneous atom transfer radical polymerization

AU Patten, Timothy E.; Xia, Jianhui; Abernathy, Teresa; Matyjaszewski, Krzysztof

CS Department Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213, USA

SO Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) (1996), 37(1), 575-6

CODEN: ACPPAY; ISSN: 0032-3934

DT Journal

LA English

AB Radical polymn. processes can yield well-defined polymers that heretofore could only be obtained through anionic polymns. The ATRP [atom transfer radical polymn.] technique involves [2,2'-bipyridyl] ligands that solubilize copper halides in the polymn. medium, and yields polymers with polydispersity of 1.05 or less, while maintaining the living nature of the polymn. In a typical ATRP of styrene, either 1-phenylethyl chloride or bromide is used as

initiator, and a mixt. of CuCl or CuBr and 2,2'-bipyridyl is the catalyst. The soly. of the Cu halide was enhanced when 4,4'-alkyl substituted bipyridyls were used. Thus with ATRP, radical polymn. can be used in the design and prepn. of well-defined materials and structurally complex macromols.

L1 ANSWER 7 OF 12 CA COPYRIGHT 1996 ACS

AN 124:317996 CA

TI From hyperbranched to crosslinked polymers by atom transfer radical polymerization

AU Gaynor, Scott G.; Edelman, Shane Z.; Matyjaszewski, Krzysztof

CS Mellon Institute, Carnegie Mellon University, Pittsburgh, PA, 15213, USA

SO Polym. Mater. Sci. Eng. (1996), 74, 236-7

CODEN: PMSEDG; ISSN: 0743-0515

DT Journal

LA English

AB Branched and hyperbranched polymers were prepd. by atom transfer radical polymn. The hyperbranched polymer was prepd. by homopolymn. of an AB<sub>2</sub>-type monomer (with 2 functional groups), such as p-chloromethylstyrene (I) in the presence of Cu(I) initiator. The branched polymer was prepd. by copolymn. of I with styrene under the same conditions. Formation of crosslinked gels occurred when either of the polymns. was carried out for long periods of time. The living nature of the polymn. is discussed, and some characteristics of the polymers are given.

L1 ANSWER 8 OF 12 CA COPYRIGHT 1996 ACS

AN 124:87826 CA

TI Atom transfer radical polymerization (ATRP): A new approach towards well-defined (co)polymers

AU Wang, Jin-Shan; Greszta, Dorota; Matyjaszewski, Krzysztof

CS Department Chemistry, Carnegie Mellon University, Pittsburgh, PA, 15213, USA

SO Polym. Mater. Sci. Eng. (1995), 73, 416-17

CODEN: PMSEDG; ISSN: 0743-0515

DT Journal; General Review

LA English

AB A review with 8 refs. on the use of ATRP to produce well-defined polymers.

L1 ANSWER 9 OF 12 CA COPYRIGHT 1996 ACS

AN 124:87825 CA

TI Transition metal catalyzed atom transfer



radical polymerization (ATRP): Principle and mechanism

AU Wang, Jin-Shan; Matyjaszewski, Krzysztof  
CS Mellon Institute, Carnegie Mellon University, Pittsburgh, PA, 15213, USA  
SO Polym. Mater. Sci. Eng. (1995), 73, 414-15  
CODEN: PMSEDG; ISSN: 0743-0515  
DT Journal; General Review  
LA English  
AB A review with 11 refs. on the principles and mechanism of ATRP.

L1 ANSWER 10 OF 12 CA COPYRIGHT 1996 ACS

AN 123:257535 CA

TI Controlled/"Living" Radical Polymerization. Halogen Atom Transfer Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process

AU Wang, Jin-Shan; Matyjaszewski, Krzysztof  
CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA, 15213, USA  
SO Macromolecules (1995), 28(23), 7901-10  
CODEN: MAMOBX; ISSN: 0024-9297  
DT Journal  
LA English  
OS CJACS  
AB An extension of atom transfer radical addn., ATRA, to atom transfer radical polymn., ATRP, provided a new and efficient way to conduct controlled/. By using a simple alkyl halide, R-X (X = Cl and Br), as an initiator and a transition metal species complexed by suitable ligand(s), Mtn/Lx, e.g., CuX/2,2'-bipyridine, as a catalyst, ATRP of vinyl monomers such as styrenes and (meth)acrylates proceeded in a living fashion, yielding polymers with d.p. predetd. by  $\Delta[M]/[I]_0$  up to Mn .apprxeq. 105 and low polydispersities,  $1.1 < Mw/Mn < 1.5$ . The participation of free radical intermediates was supported by anal. of the end groups and the stereochem. of the polymn. The general principle and the mechanism of ATRP are elucidated. Various factors affecting the ATRP process are discussed.

L1 ANSWER 11 OF 12 CA COPYRIGHT 1996 ACS

AN 123:229035 CA

TI "Living"/Controlled Radical Polymerization. Transition-Metal-Catalyzed Atom Transfer Radical Polymerization in the Presence of a Conventional Radical Initiator

AU Wang, Jin-Shan; Matyjaszewski, Krzysztof

CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA,  
15213, USA

SO Macromolecules (1995), 28(22), 7572-3

CODEN: MAMOBX; ISSN: 0024-9297

DT Journal

LA English

OS CJACS

AB A novel type of atom transfer radical polymn., ATRP, initiated with AIBN/cuIICl<sub>2</sub>/bpy affords the bulk polymn. of styrene at 130.degree. in a "living"/controlled manner, similar to the one with R-X/CuI/bpy reported earlier. Moreover, a "living"/controlled ATRP of Me acrylate at 130.degree. was accomplished, when a catalytic amt. of AIBN (1% molar equiv.) was combined with 2-chloropropionitrile (initiator) in the presence of bpy/CuIICl<sub>2</sub>.

L1 ANSWER 12 OF 12 CA COPYRIGHT 1996 ACS

AN 122:315212 CA

TI Controlled/"living" radical polymerization. atom

transfer radical polymerization in the  
presence of transition-metal complexes

AU Wang, Jin-Shan; Matyjaszewski, Krzysztof

CS Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA,  
15213, USA

SO J. Am. Chem. Soc. (1995), 117(20), 5614-15

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CJACS-IMAGE; CJACS

AB Atom transfer radical polymn. of styrene and Me acrylate is investigated using 1-phenylethyl chloride as a chlorine atom transfer precursor (initiator) and CuCl/2,2'-bipyridine complex as a chlorine atom transfer promoter (catalyst). The "living" radical polymn. of styrene alone generates polymers with predetd. mol. wt. up to Mn .apprxeq. 105 and with narrow mol. wt. distribution. Block copolymers of styrene and Me acrylate are also synthesized using the same technique.